

CLAIMS

WE CLAIM:

1. A process for removing residues from a semiconductor substrate, comprising the steps:
 - providing a densified fluid wherein said fluid is a gas at standard temperature and pressure and wherein the density of the fluid is above the critical density;
 - providing a cleaning component;
 - intermixing said densified fluid and said cleaning component whereby a reactive cleaning fluid is formed comprising reactive reverse-micelle(s) or reactive aggregates; and
 - contacting a residue on a substrate with said reactive cleaning fluid for a contact time t_c whereby said residue is chemically modified and removed from said substrate.
2. The process according to claim 1, wherein said cleaning component is selected from the group consisting of at least one reverse micelle-forming surfactant, at least one reverse micelle-forming co-surfactant, at least one reactive reverse micelle-forming surfactant or reactive reverse micelle-forming co-surfactant, at least one reactive chemical agent, and combinations thereof.

3. The process according to Claim 2, wherein said co-surfactant is an alkyl acid phosphate, alkyl acid sulfonate, alkyl alcohol, substituted alkyl alcohol, perfluoroalkyl alcohol, dialkyl sulfosuccinate, bis-(2-ethyl-hexyl) sulfosuccinate, AOT, sodium AOT, ammonium AOT, derivatives, salts, and functional equivalents thereof.
4. The process according to Claim 2, wherein said co-surfactant is a non-CO₂-philic surfactant used in conjunction with a CO₂-philic surfactant.
5. The process according to Claim 1, further comprising the step of rinsing said substrate with a densified rinsing fluid comprising up to about 30% modifiers by volume.
6. The process according to Claim 5, wherein said rinsing fluid is the pure densified fluid.
7. The process according to Claim 5, wherein said rinsing fluid is a mixture of densified CO₂ and a modifier selected from the group consisting of iPrOH, H₂O, MeOH, EtOH, or combinations thereof.
8. The process according to Claim 7, wherein said rinsing fluid comprises up to about 15% by volume iPrOH.

9. The process of Claim 1, wherein said densified fluid is a liquid with a temperature from about 20 °C to 25 °C inclusive, a pressure from about 850 psi to 3000 psi inclusive, and a density above a critical density for the densified fluid.

10. The process according to Claim 1, wherein said chemical modification of said residue comprises at least one reaction selected from the group consisting of chemical, oxidation, reduction, molecular weight reduction, fragment cracking, exchange, association, dissociation, or combinations thereof whereby dissolution, solubilization, complexation, or binding of residues occurs whereby said residues are removed from said substrate.

11. The process according to Claim 1, wherein said reactive cleaning fluid has a reduced density in the range from about 1 to 3 inclusive.

12. The process according to Claim 1, wherein said reactive cleaning fluid has a temperature and pressure above the critical temperature and critical pressure of said densified fluid.

13. The process according to Claim 1, wherein said densified fluid is a member selected from the group consisting of carbon dioxide, chlorodifluoromethane, ethane, ethylene, propane, butane, sulfur hexafluoride, ammonia, and combinations thereof.

14. The process according to Claim 1, wherein said reverse micelle forming surfactant is a member selected from CO₂-philic, anionic, cationic, non-ionic, zwitterionic, and combinations thereof.

15. The process according to Claim 14, wherein said anionic reverse-micelle forming surfactant is selected from the group consisting of PFPE surfactants, PFPE carboxylates, PFPE sulfonates, PFPE phosphates, alkyl sulfonates, bis-(2-ethyl-hexyl) sulfosuccinates, sodium bis-(2-ethyl-hexyl) sulfosuccinate, ammonium bis-(2-ethyl-hexyl) sulfosuccinate, fluorocarbon carboxylates, fluorocarbon phosphates, fluorocarbon sulfonates, and combinations thereof.

16. The process according to Claim 14, wherein said cationic reverse-micelle forming surfactant is selected from the tetraoctylammonium fluoride class of compounds.

17. The process according to Claim 14, wherein said non-ionic reverse-micelle forming surfactant is selected from the poly-ethyleneoxide-dodecyl-ether class of compounds.

18. The process according to Claim 14, wherein said zwitterionic reverse-micelle forming surfactant is selected from the alpha-phosphatidyl-choline class of compounds.

19. The process of Claim 1, wherein said reactive chemical agent is selected from the group consisting of mineral acids, fluoride-containing compounds and acids, organic acids, oxygen-containing compounds, amines, alkanolamines, peroxides, chelates, ammonia, and combinations thereof.

20. The process according to Claim 19, wherein said mineral acids are selected from the group consisting of HCl, H₂SO₄, H₃PO₄, HNO₃, HSO₄⁻, H₂PO₄, HPO₄²⁻, phosphate acids, acid sulfonates, their dissolution products, their salts, and combinations thereof.

21. The process according to Claim 19, wherein said fluoride-containing compounds and acids are selected from the group consisting of F₂, HF, dilute HF, UdHF, and combinations thereof.

22. The process according to Claim 19, wherein said organic acids are selected from the group consisting of sulfonic acids, phosphate acids, phosphate esters or their salts, their substituted derivatives, and combinations thereof.

23. The process according to Claim 19, wherein said oxygen-containing compounds are selected from the group consisting of O₂, ozone, functional or reactive equivalents, and combinations thereof.

24. The process according to Claim 19, wherein said alkanolamine is an ethanolamine.
25. The process according to Claim 19, wherein said amine is hydroxylamine.
26. The process according to Claim 19, wherein said chelate is a member of the group consisting of pentanediones; 2,4 pentanediones; phenanthrolines; 1,10 phenanthroline; EDTA, sodium EDTA, oxalic acid, or combinations thereof.
27. The process according to Claim 19, wherein said peroxides are selected from the group consisting of organic peroxides, alkyl peroxides, t-butyl peroxides, hydrogen peroxide, substituted derivatives, and combinations thereof.
28. The process in accordance with Claim 1, wherein said reactive cleaning fluid comprises up to about 30% by volume of reactive reagents and/or modifiers.
29. The process in accordance with Claim 28, wherein said reactive cleaning fluid comprises about 2 to 5% modifiers by volume including PFPE acid phosphate, AOT, H₂O, or combinations thereof.
30. The process in accordance with Claim 28, wherein said reactive cleaning fluid comprises about 3 to 5% modifiers by volume including PFPE carboxylate, alkanolamines, hydroxylamine, H₂O, or combinations thereof.

31. The process in accordance with Claim 28, wherein said reactive cleaning fluid further comprises a corrosion inhibitor having a concentration in the range from about 0.1% to 1% inclusive by volume.

32. The process in accordance with Claim 31, wherein said corrosion inhibitor is selected from the group of benzotriazoles; 1,2,3-benzotriazole; catechols; catechol; 1,2-di-hydroxy-benzene; 2-(3,4-di-hydroxy-phenyl)-3,4-di-hydro-2H-1-benzopyran-3,5,7-triol, substituted derivatives, and combinations thereof.

33. The process according to Claim 28, wherein said reactive cleaning fluid further comprises about 5% modifiers by volume including PFPE carboxylates, amines, alkylamines, hydroxylamine, benzotriazoles, catechols, and combinations thereof.

34. The process of Claim 1, wherein time t_r is about 15 minutes inclusive.

35. The process of Claim 1, wherein time t_r is less than about 5 minutes.

36. The process of Claim 1, wherein said residue is selected from the group consisting of organic residues, metal residues, etch residues, non-metal residues, polymeric residues, and combinations thereof.

37. The process of Claim 1, wherein said residue is a transition metal.

38. The process of Claim 1, wherein said residue is selected from the group consisting of Cu, Al, Fe, Ta, and combinations thereof.

39. The process of Claim 1, wherein said reactive cleaning fluid has a temperature of about 20 °C to 25 °C, a pressure of about 850 to 3000 psi, and a fluid density above the critical density of the densified fluid.